

ABSTRACTS FROM THE ORIGINAL PAPERS.

*The Chemical and Mineralogical Investigations on the
Infertile Volcanogenous Soils of the Southern
Part of the Prov. Shinano.*

By TOYOTARŌ SEKI.

The peculiar infertile soils so called "*misotsuchi*" extending at the surface and some centimetres below the surface in the higher parts of the Tenryūgawa Valley (T. V.) and at the southern skirt of the Yatsugatake Volcanoe (Y. S.) were investigated in the laboratory of Central Agricultural Experiment Station and the brief summary will be given here.

The soils form the uppermost parts of the old quarternary formation covering the thick strata consisting of the fluvial gravels.

Their inner structures and adjacent topographies suggest that the soils are the *lacustrine* deposits of the later diluvial age. From the modes of occurrence and the results of microscopical observations it is clear that they were originally the fine porous *pumiceous volcanic ejectaments* of the andesitic character, which have undergone the decomposition at first under the shallow waters and then at the land surface.

The soils naturally wet exhibit the light reddish brown colours with somewhat spongy structures. The water held by them cannot easily be removed by exposing them to the air in open place in the shadow. When air-dried, they exhibit the faint brownish yellow colours becoming the light porous and fragile fragments which give readily the fine powders on rubbing. If the half-dried fragments are stirred in the water they give the thick turbid liquids which remain almost unchanged for few

days showing the high grades of *colloidal*ity, which give rise to the strong retentive powers of the soils for water.

The air-dried and shifted samples were treated with boiling 20 per cent hydrochloric acid and the substances decomposed by the acid were determined quantitatively.

The results of analyses are as follows :-

	Subs. dec. by HCl	Residue undec.	Water above 100°	Water below 100°	Total Sum
The Soil of Fujimi (Y. S.)	36.72	23.99	11.71	27.72	100.14
The Soil of Ijima (T. V.)	42.68	7.53	13.43	36.26	99.90

The substances decomposed by the hydrochloric acid are constituted of :-

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
The Soil of Fujimi	14.43	19.36	1.97	0.05	0.04	0.16	0.12	0.08
The Soil of Ijima	17.21	22.23	2.20	0.05	0.10	0.17	0.05	0.08

The minor ingredients were omitted here.

The large amounts of the hygroscopic moisture and the substances decomposed by hydrochloric acid and the great deficiencies in lime, potash and phosphoric acid must be carefully noticed. The molecular ratios of the most important ingredients to alumina calculated for our samples and some other soils are given in the following table :-

	Volc. Soil of Fujimi	Volc. Soil of Ijima	Acid Soil of Mino	Volc. Soil of Tokyo
SiO ₂	1.26	1.31	1.20	1.63
Al ₂ O ₃	1.00	1.00	1.00	1.00
Fe ₂ O ₃	0.07	0.07	0.26	0.36
MgO	0.01	0.01	0.09	0.23
CaO	0.00	0.01	0.01	0.04
Na ₂ O	0.01	0.01	0.02	0.02
K ₂ O	0.01	0.00	0.02	0.02
P ₂ O ₅	0.00	0.00	0.01	0.00

The molecular ratios of the total alkaline bases to alumina in our samples are far less than that in the infertile acid soil of the Prov. Mino and represent the minimum value among the numerous volcanogenous soils hitherto investigated by the author. The molecular ratios of silica to alumina in our soils approach to those

in the *lateritic* soils.

The both soils are stained vividly red by acid fuchsin and light bluish green by methylene blue, that is they are distinctly *oxyphilous* and *basophilous* (amphophilous). The facts explain that the soils contain both positive colloids (oxyphilous) and negative colloids (basophilous). The two dyes absorbed by the soils were also colorimetrically determined. The quantities of alumina extracted almost free from silica with 10 per cent sodium carbonate solution by the author's method amount to about 3 per cent. The last fact together with the distinct oxyphilous character prove that the soils contain *free alumina* in the form of colloidal hydroxide. The ferric oxide in the soils will mostly be in the form of limonite which is almost indifferent to the aniline dyes. From these reasons the author assumes that the main parts of our samples are constituted of the large quantities of *colloidal clays*, smaller quantities of active *colloidal aluminium hydrate* and less quantities of inert ferric oxide (*limonite*). The presence of free aluminium hydrate shows that the soils are proceeding a step into the *lateritic phase* of weathering, as is suggested by the low values of the molecular ratios $\text{SiO}_2 : \text{Al}_2\text{O}_3$.

The two soils do not exhibit the acid reaction to test paper notwithstanding they are very rich in the colloidal clays and exceedingly poor in alkaline bases. The fact can be explained by the presence of the active gels of aluminium hydrate which "*compensate*" the acid reaction of colloidal clays, as was demonstrated by the author's preliminary experiments. The soils exert — very *high absorptive powers* for ammonia and phosphoric acid and these facts can also be explained by the presence of colloidal clays and aluminium hydrate. In such soils ammonia, potash and phosphoric acid given as fertilizers in ordinary doses are liable to be converted into the unavailable forms.

The unproductiveness of our soils due chiefly to the defect in physical properties and the lack of mineral nutrients. The improvements will be accomplished (1) by the liming and deep cultivation in order to coagulate the colloidal substances and produce the granular structures, (2) by the rich supply of superphosphate and potash salts and the adequate addition of nitrogenous manures, (3) by the propagation of

reguminous green-manure plants in order to enrich the soils with humus and organic nitrogen. The practical applications of those methods must carefully be verified by preliminary field experiments.

*On the Chemical Constitution of the Cocoon Silk
and the Sericin of the Cocoons of
Antheraea Yamamai.*

By RYŪGO INOUE and MASARU HIRASAWA.

I. The Chemical Constitution of the Cocoon Silk.

(a) The General Composition.

The cocoons were get at Ariake-mura, Minamiazumi-gun, Nagano-ken, and analyzed with the following results, after having get rid of the impurities.

Water	10.77	%
Total nitrogen	16.51	"
Ash	4.15—5.00	"

Lime is a predominant constituent in the ash and exists mostly in the form of oxalate in the cocoons.

The various forms of nitrogen in the hydrolysate of the cocoon silk with concentrated hydrochloric acid, were determined as follows :—

	In 100 g of the anhydrous cocoon silk.
Total nitrogen	16.51 g
Nitrogen dissolved in conc.HCl	16.37
Nitrogen precipitated by phosphotungstic acid	3.07
Nitrogen not precipitated by phosphotungstic acid	12.82
Nitrogen in the form of ammonia	0.22
Nitrogen in the melanine resulted by hydrolysis	0.18
In the nitrogen precipitated by phosphotungstic acid,	
Arginine nitrogen	0.10
Histidin nitrogen	0.18
Lysine nitrogen	1.14

(b) Total Hydrolysis.

200 grms. of the cocoon silks were hydrolyzed with 2500 c.c. of concentrated hydrochloric acid. After 12 hours' boiling the hydrolysate ceased to show biuret reaction, and then amino-acids were separated by the ester method with the following results.

Amino acid	In 100 grms of anhydrous cocoon silk.
	In grm.
Glycocoll	17.83
Alanine	20.16
Leucine	1.23
Aspartic acid	0.26
Glutamic acid	Trace
Serine	2.83
Proline	0.21
phenylalanine	0.22
Tyrosine	5.34

Tyrosine was separated by another way as follows:- 50 g of the cocoon silk were hydrolyzed with 30% sulphuric acid for 12 hours until the hydrolysate has not shown biuret reaction. Then the sulphuric acid was exactly removed by concentrated solution of baryta. The precipitate of barium sulphate thus produced was filtered, and so often washed until the washing did not react with the Millon's reagent. The filtrate and washings were united together and decolourized with animal charcoal. And the solution thus purified was evaporated until tyrosine was crystallized out. It was filtered after standing for 24 hours. The filtrate of tyrosine was evaporated, and the remaining tyrosine was obtained.

These amino acids thus separated were determined by analysis.

II. The Chemical Constitution of the Sericin of the Cocoons.

(a) The Separation of Sericin.

10000 cocoons of Yamamai-moths were cut in two and the chrysalis, the skins casted, and other impurities were removed. The cocoons thus purified, were digested with 40% alcohol in an autoclave under 0.5 atmospheric pressure. The green pigment of the cocoons was dissolved in the alcohol. The cocoons were treated twice in the

same way, and thus decolourized nearly in white. Then they were digested again under 1 atmospheric pressure for 30 minutes with steam, and filtered through a Buchner-funnel by means of sucking down by a vacuum produced by a filter pump. The filtrate was evaporated into a syrup after having been filtered once more, and dried up on concentrated sulphuric acid. After completely drying, the sericin was ground into powder. The yield of the sericin was 200 grams from 5000 grams of cocoon silk. The sericin thus obtained, contained 3.12% water, 16.85% the total nitrogen, and 1.00% ash.

200 grams of the sericin were hydrolyzed by 2000 c.c. of 30% sulphuric acid. After 78 hours' boiling the hydrolysate ceased to show biuret reaction. The sericin was completely dissolved without any residue. Then tyrosine was at first separated by the same method described as before. From the filtrate of tyrosine other amino acids were separated by the usual method. The amino acids thus obtained were determined by analysis.

The results of the total hydrolysis were as follows :-

Amino acids	In 100 grams of anhydrous sericin.
Glycocoll	3.45 g
Alanine	3.99
Leucine	1.50
Serine	4.38
Aspartic acid	2.96
Glutamic acid	presence
Phenylalanine	2.04
Tyrosine	4.33
Proline	presence

III. Conclusion.

By comparing the chemical constitution of the Yamamai cocoon silk to those of the tussah produced at the same district, and of "Kinjō-matamukashi" cocoon silk (one of Japanese domesticated silk-worm), the following table is obtained.

Amino acids	Yamamai-cocoon silk.	Tussah-cocoon silk.	Kinjō-matamukashi cocoon silk.
Glycocoll	27.83 %	12.34 %	29.39 %

Alanine	20.16	15.27	16.72
Leucine	1.23	0.27	1.47
Aspartic acid	0.26	2.37	0.03
Glutamic acid	+	+	0.023
Serine	2.83	0.55	3.01
Proline	0.21	0.26	1.106
Tyrosine	5.34	6.62	4.72
Phenylalanine	0.22	0.37	0.64

From the above results glycocoll, alanine and tyrosine are predominant amino acids in the Yamamai silk, as general in the silk, and it stands nearer to the true silk in the chemical composition, than the tussah silk. But that more aspartic acid is contained, when compared to the true silk, and alanine is more in quantity than glycocoll, is similar to the tussah silk. From those facts the Yamamai-silk may be said to stand in the middle point between the true and tussah silk in the chemical composition.

The chemical composition of the sericin of the Yamamai-silk is compared to those of the other sericins, which have been investigated until to-day, in the following table :-

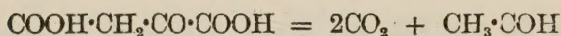
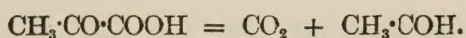
Amino acids	Sericin from Yamamai silk	Sericin from Daiwanishiki silk	Sericin from Italian silk	Sericin from Canton silk	Sericin from the European silk
Glycocoll	3.45 %	3.93 %	1.5 %	1.2 %	0.1-0.2 %
Alanine	3.99	3.53	9.8	9.2	5.0
Leucine	1.50	0.4	4.8	5.8	—
Aspartic acid	2.96	3.91	2.8	2.5	—
Glutamic acid	+	3.0	1.8	2.0	—
Serine	4.38	5.99	5.4	5.8	6.6
Proline	+	0.35	3.0	2.5	—
Tyrosine	4.33	3.27	1.0	2.3	5.0
Phenylalanin	2.04	0.49	0.3	0.6	—

From the above results the sericin of the Yamamai-silk is very much near to that of the true silk in the chemical composition. If it is the fact, the cocoons of the Yamamai-moths must be so easily reeled as those of the domesticated ones, but in practice it is not the case. The reason is probably due to that the calcium salts, contained comparatively more in quantity on the cocoons, prevent the sericin from dissolving, when the cocoons are boiled and the silk is reeled.

*Ueber die Enzymatische Spaltung der Laevulinsäure
(Ein Beitrag zur Wirkung der Carboxylase).*

VON KANROKU KURONO, TÖSHI FUKAI und SEIJUN TATENO.

Nach C. Neuberg werden α -Ketosäuren wie Brenztraubensäure und Oxallessigsäure durch Einwirkung von Carboxylase in Kohlensäure und Azetaldehyd nach folgendem Schema gespalten.



Andere α -Ketosäuren wie α -Ketobuttersäure, α -Ketocaprinsäure, Oxybrenztraubensäure, α -Ketoglutarsäure, Phenylglyoxalsäure, Phenylbrenztraubensäure und Oxyphenylbrenztraubensäure verhalten sich gegen Carboxylase genau in derselben Weise und bilden sich dabei Kohlensäure und die entsprechenden Aldehyde.

In Oxallessigsäure und α -Ketoglutarsäure steht eine der zwei COOH Gruppen gegen CO Gruppe in β -bzw. in γ -Stelle: trotzdem werden die beiden Carboxylgruppen gleichzeitig angegriffen. So kann man vermuten, dass β -oder γ -ketosäuren ebenfalls durch Carboxylase abgespalten werden. Um diese Frage zu entscheiden, haben die Verfasser mit Laevulinsäure (γ -Ketosäure) einige Versuche angestellt und gefunden, dass es tatsächlich der Fall war.

In einem Versuche wurden 20 ccm. 0.5% iger Laevulinsäurelösung, die zuvor mit einer K_2HPO_4 -pufferlösung neutralisiert war, in einen Einhorn'schen Gärkolben gefüllt, mit 2g Trockenhefe versetzt und unter Zusatz von 0.1 % Thymol im Wärmekasten bei 25-30° stehen gelassen. Nach 48 Stunden beobachtete man, dass 27% der zugesetzten Laevulinsäure zerlegt wurden, d. h. 62% der in Lösung vorhandenen freien Säure.

Es wurde erfahren, dass der optimum PH-Wert der Lösung für die Carboxylase-Wirkung 4.5% und die optimale Konzentration der Laevulinsäure 0.5% war. 1% ige Lösung wirkte schon schädlich. Ferner wurde beobachtet, dass das Kalium oder Natriumsalz der Laevulinsäure nicht gespalten war.

Die Verfasser haben später mit grösserer Menge Laevulin-säure gearbeitet und als Spaltungsprodukte derselben Methyl-ethyl-*keton* isoliert und es als krystallinisches Semicarbazon identifiziert. So kann man den Reaktionsverlauf sich in folgender Weise vorstellen :-



Laevulinsäure

Methyl-ethyl-keton.

So bietet es ein neues Beispiel für die Wirkung der Carboxylase dar. Die Verfasser beabsichtigen die versuche mit verschiedenen β -oder γ -Ketosäuren weiter fortzusetzen. Ferner bleibt die Frage, ob es sich beim Abbau der α -und γ -Ketosäuren um eine und dieselbe Carboxylase handelt, noch zu entscheiden.

*A New Method for the Quantitative Determination of
Amylo-Liquefying Enzyme.*

By KŌKICHI ŌSHIMA and SHINICHI ITAYA.

Make 450 c.c. of starch paste with 7.5 grams (as dry matter) of purified potato starch. 18 c.c. of this paste + 2 c.c. regulating mixtures of M/6 citric acid and M/6 Na_2PO_4 to keep certain hydrogen ion concentration, and digest with 2 c.c. of enzymic solution for 30 minutes at 40°C . Then add 2 c.c. of N/2 NaOH to stop the digestion. Add again 2 c.c. of M/6 citric acid and M/6 Na_2HPO_4 , which makes it's total 2 c.c. M/6 citric acid and 2 c.c. Na_2HPO_4 . Determine the viscosity of digested liquid at 18°C with Ostwald's viscosimeter of 8 c.c. capacity in which distilled water flows down with 15.0 seconds. With this calculate the enzyme strength from the table shown below.

This table was made experimentally with different concentrations of an enzymic preparation from *Aspergillus oryzae*. When 1% solution of an enzymic sample digests 1.5% starch paste at 40°C for 30 minutes and the viscosity is 47 seconds (which is same viscosity with 1% paste) then the amyloliquefying activity is 10.

Table:- Activity Scale of Amylo-liquefying Enzyme.

Seconds of viscosity	Amylo-liquefying activity \times Y	Seconds of viscosity	Amyloliquefying activity \times Y
$\times 20$	100.0	$\times 38$	16.6
21	87.5	40	15.5
22	75.0	$\times 43$	12.5
23	62.5	45	11.2
$\times 24$	50.0	$\times 47$	10.0
25	48.0	$\times 50$	8.3
26	46.1	$\times 53$	6.3
$\times 27$	40.0	$\times 55$	5.0
$\times 28$	33.3	57	4.8
29	28.0	$\times 60$	3.1
30	27.0	$\times 62$	2.5
31	26.0	$\times 65$	1.6
$\times 32$	25.0	67	1.5
33	22.5	$\times 69$	0.8
$\times 34$	20.0	$\times 72$	0.4
35	19.4	$\times 75$	0.2
36	18.8	$\times 81$ (no digestion)	0.0

N. B. Y = % of enzymic solution.

\times = experimental value.

This table can be used for amylases from molds and grains, as the experiment with malt amylase showed almost same result. If a viscosimeter of different flowing velocity is used, then this table can be used by calculating relative velocity.

This method is quite convenient, and accurate, and is used by the authors for the comparison of many kinds of germinated and ungerminated grains and molds.